"Express Mail" mailing label number EV 327 129 049 US

Date of Deposit: April 8, 2004

Case No. 11909-4

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
APPLICATION FOR UNITED STATES LETTERS PATENT

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TITLE: FABRICATION OF NANOSTRUCTURES

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FABRICATION OF NANOSTRUCTURES

CROSS REFERENCE TO RELATED APPLICATIONS

[001] This application claims priority to U. S. Provisional Application No. 60/462,049, filed April 11, 2003, entitled "Fabrication of Nanostructures," the entire contents of which are incorporated herein by reference.

BACKGROUND

[002] The field of nanotechnology has evolved out of the desire to maintain Moore's la w, which states that the storage capacity of silicon based integrated circuits should double every eighteen months. Other fields such as micro-electromechanical systems (MEMS), photonics, displays for cellular phones, and personal media have benefited from the semi-conductor industries technological breakthroughs.

[003] The diffraction limit of the light presently used in photolithography threatens to prevent conventional methods from forming sub-100 nanometer (nm) structures. Thus, alternative technologies for the fabrication of nanostructures, including, but not limited to nanowires and nanoarrays, are needed to replace or augment conventional lithographic techniques for the fabrication of semiconductors.

[004] Alternative technologies have emerged that may produce sub-100 nm structures. These methods include electron beam lithography, X-ray photolithography, extreme ultraviolet photolithography, focused ion beam, microcontact printing, nanoimprint lithography, as well as variants of the serial scanning probe microscopy nanolithographies (e.g. dip-pen nanolithography). Advances in these fields may eventually lead to higher

density semiconductor chips with smaller circuits having faster computational speed and signal transfer.

[005] However, each of these existing technologies has disadvantages. While X-ray photolithography may be a promising avenue for large volume mass production of sub-100 nm structures, the direct write photomasks required for parallel processing are very expensive. Furthermore, the production of sub-100 nm structures is difficult to achieve in a parallel manner. Alternative methods for generating low cost X-ray masks would be beneficial.

[006] It would be desirable to have a method for the fabrication of metal, ceramic, and polymeric nanostructures. It would also be beneficial to have a process for making these structures that was easy to scale up and suitable for industrial scale manufacturing. The present invention overcomes at least one disadvantage of prior nanofabrication methods by providing a more direct method involving fewer processing steps, and affords both a greater range of structural size and the ability to further manipulate the product geometries.

SUMMARY OF THE INVENTION

[007] The present invention relates to nanostructures and the fabrication of nanostructures, such as nanowires and nanoarrays. In one aspect, the synthesis of the nanostructures may include the mechanical deformation of a film combined with the chemical modification of the film. Mechanical deformation may be provided by contacting and compressing a stamp having raised and recessed regions into the film. Optionally, the deformed material may be transferred to a support. In another aspect, the present invention may include stamps and the production of stamps that

include embedded nanostructures that may be placed on a photoresist and irradiated.

[008] The resultant nanostructures and the nanoscale production methods utilized to produce them may beneficially be used in catalysis, soft lithography, sensors, elements for the construction of nanocircuits, photonics, displays, X-Ray stencils, band-gap devices, and nanocomputers, for example.

[009] Other systems, methods, features and advantages of the invention will be, or will become, apparent to one with skill in the art upon examination of the following figures and detailed description. It is intended that all such additional systems, methods, features and advantages be included within the description, be within the scope of the invention, and be protected by the following claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The invention can be better understood with reference to the following drawings and description. The components in the figures are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention. Moreover, in the figures, like references numerals designate corresponding parts throughout the figures.

[0011] **FIG. 1** illustrates a procedure for fabrication of nanostructures embodying aspects of the present invention.

[0012] **FIG. 2** illustrates an exemplary procedure illustrating several products fabricated according to the invention.

[0013] FIG. 3 illustrates a procedure embodying aspects of the present invention where a nanostructure of the present invention is used as a mask for a lithographic process.

[0014] FIG. 4 illustrates a procedure for the directed transfer of a nanostructure to a support embodying aspects of the present invention.

[0015] FIG. 5a illustrates a stamp having sloped sidewall geometry ("saw to oth") with the angle of sidewall slope depicted by a dashed line.

[0016] FIG. 5b illustrates a stamp having "recta ngular" side wall geometry.

[0017] FIG. 6 illustrates a compression cell having planar compression plates as may be utilized to fabricate nanostructures in accordance with the present invention.

[0018] FIG. 7 illustrates a compression cell having curved compression plates as may be utilized to fabricate nanostructures in accordance with the present invention.

[0019] FIG. 8 depicts nanostructures embodying aspects of the present invention where gold nanowires were fabricated and then transferred to a support already possessing gold wires to create a gold crosshatch pattern.

[0020] **FIGs. 9a-b** depict nanostructures embodying aspects of the present invention where a three-layer gold nanowire crosshatch was fabricated by the successive transfer of nanowires to a support.

[0021] **FIG. 10** depicts nanostructures embodying aspects of the present invention where gold nanowires were fabricated on the raised regions of a stamp and gold nanowires also were fabricated within the recessed regions of the stamp.

[0022] **FIG. 11** depicts nanostructures embodying aspects of the present invention where gold nanowires were fabricated on the raised regions of a stamp and colloidal latex beads were deposited in the recessed regions of the stamp for illustrative purposes.

[0023] **FIG. 12** depicts nanostructures embodying aspects of the present invention where gold nanowires are fabricated whose width varies radially.

DETAILED DESCRIPTION

[0024] **FIGs. 1a-c** illustrate a preferred process for fabricating nanostructures, such as nanowires, in accordance with the present invention. In **FIG. 1a**, stamp **7** may be contacted with film **8**, which may reside on an optional supporting substrate **9**. The stamp **7** may possess one or a plurality of raised regions **5** and one or a plurality of recessed regions **6**. At least one of the raised regions **5** may form a contact **10** with the film **8**. The raised and recessed regions may alternate continuously in one, two, and/or three dimensions or their alternating pattern may stop and restart in a different position, thus being discontinuous in one or more of the three dimensions.

As used in the specification and appended claims, "on" includes when films are adjacent to the supporting substrate and when films are separated from the supporting substrate by one or more intervening films or layers.

[0025] The smallest feature dimension of the stamp **7** is preferably from 1 to 5000 nm. More preferably, the smallest feature dimension of the stamp **7** may be from 20 to 1000 nm. A feature dimension of the stamp is defined as the distance from one portion of a raised region to the same portion of an adjacent raised region. In addition to the smallest feature dimension, the stamp **7** may include features having dimensions that are significantly larger than the smallest feature dimension.

[0026] The stamp **7** may be made from any material or combination of materials having sufficient mechanical strength to bring about deformation of the film **8**. In one aspect, materials having a Young's Mod ulus of at least 10^7 Pascal (Pa) are used. In a preferred aspect, materials having a Young's Modulus from 10^8 to 10^{10} Pa are used. At present, materials having a Young's Mod ulus of from 2 to 4 X 10^{10} Pa, more preferably from 2.2 to 3.5 X 10^{10} Pa, are preferred.

[0027] Polymer materials for use in the stamp **7** may include thermoplastic polymers, thermosetting polymers, polymer composites, polyethylene, polystyrene, poly(methyl methacrylate), polybutadiene, polypropylene, and combinations thereof in either amorphous or crystalline states. Preferable polymers for use in the stamp **7** include polycarbonate, polyethylene, polystyrene, poly(methyl methacrylate), polypropylene, polybutadiene, their derivatives, and their co-polymers. More preferable polymers for use in the stamp **7** include polyimide, polyphenylene oxide, polyethylene oxide, TEFLON, polydimethylsiloxane, polypropylene, as well as conductive polymers such as polythiophene, polypyrrole, and polyacetylene. Especially preferred polymers for use in the stamp **7** at

present include polycarbonate, polystyrene, poly(methyl methacrylate), and polybutadiene as available, for example, from Aldrich (Milwaukee, WI) and Scientific Polymer Products Inc. (Ontario, NY).

[0028] The material or materials from which the stamp **7** is formed may include inorganic constituents or compositions. Such stamp materials also may be a composite material that includes polymers, thermosetting polymers, co-polymers, silica particles, alumina particles, silicon nitride particles, tungsten carbide particles, silicon carbide particles, gold, tungsten, tantalum, metal oxide particles, ceramic particles, or combinations thereof.

[0029] The stamp **7** may be substantially planar, as illustrated in **FIGs. 1a-c**, or non-planar. Non-planar stamp architectures may include cylinders, cubes, pyramids, wheels, helix, discs and polygons, and the like. Furthermore, the geometry of stamp **7** may be symmetric or non-symmetric, thus possessing multiple sides of different geometries. Similarly, stamp **7** may be in the form of a disc, which is able to rotate, thus allowing continuous asymmetric or symmetric surface patterning in accordance with this invention.

[0030] The film **8** may be any mechanically deformable material, including a polymer, metal, amorphous film of organic and/or inorganic molecules, ceramic, semiconductor, alloy, self-assembled monolayer of organic and/or inorganic molecules, or combination thereof. The film **8** may include materials in the solid, gel, and/or liquid phase. At present, an especially preferred material for the film **8** includes gold and its alloys.

[0031] The supporting substrate **9** may be a solid polymer, ceramic, metal, alloy, semiconductor, or glass; a porous or nanoporous ceramic, glass, semiconductor, polymer, or thermoset; other nanoporous materials; a halogenated polymer; a gel; or any combination thereof. The term "porous"

refers to hollow regions within a material having an average internal diameter from 0.1 micrometer (μm) to 1 μm. The term "nanoporous" refers to hollow regions within a material having an average internal diameter from 1 nm to 99 nm. The supporting substrate **9** may more preferably include silicon, mica, aluminum oxide, indium tin oxide, highly oriented pyrolytic graphite, and/or glass. At present, an especially preferred material for the supporting substrate **9** is muscovite mica available from Structure Probe Inc., West Chester, PA.

[0032] The supporting substrate **9** is not required to be planar, as illustrated in **FIGs. 1a-c**, but may include other geometries such as a cylinder, cube, pyramid, wheel, helix, disc, polygon, or any combination of such geometries. In one aspect, the geometry of the stamp **7** may depend on the geometry of the film **8**, which may depend on the geometry of the supporting substrate **9**.

[0033] The surface of the supporting substrate **9** may be modified with one or more resist materials that may allow for additional photolithographic patterning of substrate **9** after formation of the nanostructures. Subjecting portions of the substrate **9** to a magnetic field can align magnetic materials on the resulting products. Subjecting portions of the substrate **9** to an electric field also can modify the resulting width of the resulting nanostructures. Subjecting the substrate **9** to radiation or chemical reagents to chemically modify the surface energy of the materials can facilitate or inhibit nanostructure formation. Subjecting the film **8**, stamp **7** and/or substrate **9** to sonication can clean the stamp and nanostructures as well as provide a means of separating the stamp **7** from the nanostructure products.

[0034] **FIGs. 1b-c** illustrate an example of what may occur as force is exerted on the stamp **7** during a stamping procedure. During the stamping procedure force is exerted on the stamp **7**, thereby, causing the mechanical

deformation of the film **8**. In one aspect, the stamp **7** may expand laterally when compressed into the film **8**. In another aspect, the stamp **7** may undergo an elastic expansion when compressed into the film **8**.

[0035] As force is applied to the film **8** at the contact **10**, concave down buckling at **15** may be contiguous to the compressive stress centered at **14**. In combination, this localized buckling can create a lower channel **12**, which may be formed between the underside of the film **8** and the supporting substrate **9**. Upper channel **11** also may be formed from deformation and/or compression of the film **8** at the contact **10** to form a buckled film surface **13** in the recessed region **6** of the stamp **7**. The upper channel **11** may be defined as a region encompassed by the inner walls of stamp **7** and the buckled film surface **13**. Multiple upper and lower channels, **11** and **12**, respectively, may be formed in this manner.

[0036] In one aspect, the force exerted on the stamp **7** may be from 10^5 to 10^{10} Pa. In a preferred aspect, when the stamp **7** is a polymer and the film **8** is a metal, the force applied to the stamp **7** may be from 10^6 to 10^8 Pa. In one aspect, the force exerted on the stamp **7** is about 380 X 10^6 Pa. At present, the force exerted on the stamp **7** is preferably greater than the yield stress of the film. In this manner the stamp **7** may completely penetrate or cut through the film **8**. In one aspect, the nanostructures may have their average cross-sections modulated by varying the force applied to the stamp **7**. In the specification and appended claims, the term average cross-section is the average of the width or height dimension of the formed nanostructures.

[0037] As the force applied to the stamp **7** increases, so will the degree of deformation that occurs in the film **8**. Therefore, the aspect ratio, defined as the ratio of nanostructure height to width, can be adjusted with the force applied to the stamp **7**. The radial distribution of elastic and/or plastic forces acting at the contacts **10** between the stamp **7** and the film **8** may allow for

the fabrication of nanostructures whose width can vary radially from the center of contact, as will be discussed in greater detail with regard to **FIG. 7**. The force required to form a nanostructure having a given height and width may be estimated using several theories known to those of ordinary skill in the art. A detailed treatment of these theories may be found in H. Hertz, et al., *J. Reine Angew. Math.*, p. 156 (1881) (Hertzian theory of elastic compression); K. L. Johnson, *Contact Mechanics*, p. 125 (1987)) (contact mechanics theories).

[0038] The structure resulting from the stamping procedure, a combined stamp/film/supporting substrate "s andwich" may then be immersed or exposed to a chemical reagent (not shown), such as an etchant. For example, if the film **8** is metal, a metal etchant may be used to dissolve or react with a portion of the metal film. The chemical reagent may be a liquid, gas, solution, gel, dispersion, and/or slurry and may be allowed to diffuse, or may be alternately forced, through the upper and/or lower channels. In this manner, portions of the film may be removed through the etching process.

[0039] The upper and lower channels may have distinct surface energies or surface tensions in response to the materials from which the stamp **7**, the film **8**, and the supporting substrate **9** are fabricated. The surface energies and/or surface tensions of the channels may be affected by their hydrophilic character, hydrophobic character, mechanical forces, and the like. These mechanical forces may include a tangential sheer stress generated by the lateral expansion of the stamp when compressed.

[0040] The type of interaction the chemical reagent has with the surface energies of the channels **11**, **12** may be referred to as an anisotropic interaction. Thus, the selective reaction of a chemical reagent with the film **8** in the lower channel **12** may occur, while the chemical reagent is substantially excluded from the upper surface of the film **8** present in the

upper channel **11**. In one preferred aspect, the upper channel **11** or the lower channel **12** may be etched to the substantial exclusion of the other.

[0041] For example, if the stamp **7** is a hydrophobic material (e.g. plastic), the film **8** is a metal (e.g. gold), and the supporting substrate **9** is a hydrophilic material (e.g. oxidized Si or muscovite mica), a water based (hydrophilic) etchant may be used to favor etching the concave down portion **15** of the metal above the lower channel **12**, while substantially excluding etching in the upper channel **11**. Thus, when the supporting substrate **9** is hydrophilic in nature, the stamp is less-hydrophilic in nature, and a water-based etchant is utilized, etching may selectively occur at a more rapid rate in the lower channel **12**. Conversely, a hydrophilic etchant may selectively etch in the upper channel **11** in a more rapid manner, to the substantial exclusion of the lower channel **12**. Furthermore, as the etching process continues, the film **8** may be pushed further into the upper channel **11** of the stamp **7**, as is illustrated in the progression from **FIG. 1b** to **FIG. 1c**.

[0042] Due to the many combinations of hydrophilic and less-hydrophilic materials that may be used as the stamp **7**, the film **8**, the supporting substrate **9**, and the etchant, many variations are possible within the scope of the invention. Thus, one of ordinary skill in the art may maximize the likeness or difference between the surface energies of the upper and lower channels, **11** and **12**, respectively, to facilitate a substantially channel selective processes.

[0043] Many types of nanostructures may be fabricated using the basic methodology represented by **FIG. 1** due to the ability to simultaneously control multiple variables. These variables include the extent of etching; the technique used to separate the stamp **7** from the supporting substrate **9**; and the adhesive and mechanical forces acting at the contacts **10** between the stamp **7** and the film **8**, and between the film **8** and the supporting substrate

9. These and other variables may be controlled through the selection of the materials used, the pressures applied to the stamp **7**, and/or the chemical reagent, as would be known to one of ordinary skill in the art.

[0044] For example, adjusting the solvent composition of the chemical reagent can determine whether both the upper and lower channels **11**, **12** or one of the channels preferentially undergoes chemical reaction. Adjusting the temperature during fabrication can increase the rate of structure formation and influence the organization and average cross-section of the resultant nanostructures. Adjusting the geometry of the raised region **5** in the stamp **7** can direct the placement of the nanostructures on the stamp **7** and/or on the supporting substrate **9**. Adjusting the geometry of the recessed region **6** in the stamp **7** also can direct the placement of the nanostructures on the stamp **7** and/or on the supporting substrate **9**. Adjusting the force applied to the stamp **7** can influence the average cross-section of the nanostructures formed on the stamp **7** and/or the supporting substrate **9**. Changing the material of the stamp **7** may influence the average cross-section of the nanostructures formed on the stamp **7**, may influence the dimensions of the nanoscopic deformations that the stamp itself undergoes during compression, may influence the dimensions of the nanoscopic deformations of the film **8** during compression, may influence the adhesion of the formed nanostructures to the stamp **7**, and may influence the optical properties of the stamp **7**. Changing the material of the film **8** can vary the resulting materials to be patterned. Adjusting the materials of the supporting substrate **9** may change the physiochemical interactions with the film **8** and may influence the average cross-section and placement of the formed nanostructures.

[0045] **FIG. 2** illustrates a variety of nanostructures that may be fabricated in accordance with the present invention. When a nanostructure fabrication procedure, such as previously discussed with regard to **FIG. 1**, is

complete, the location of fabricated nanostructures **213** and **214** are shown in structure **200**. The nanostructures **213** and **214** may be portions of the film **8** that where not removed by the etchant.

[0046] The nanostructure **214** may be formed at the point of contact **14** between the stamp **7** and the film **8** (**FIG. 1c**). The nanostructure **213** may be formed within the recess region **6** of the stamp **7** (**FIG. 1a**). In one aspect, the nanostructure **213** may have an average cross-section that is larger than the nanostructure **214**. In another aspect (not shown), the nanostructure **214** may have an average cross-section that is larger than nanostructure **213**. Furthermore, the average cross-sections of the nanostructures **213** and **214** may be substantially equal. In one aspect, the average cross-section of the resulting nanostructures may range from 1 nm to 1 μm, preferably from 1 nm to 500 nm, and more preferably, from 1 nm to 100 nm. At present, preferred nanostructures have average cross-sections from 500 nm to 1 μm or less than 120 nm.

[0047] Upon separation of the stamp **7** from the supporting substrate **9**, structures **210, 220, 230, 240, 250,** and **260** may result. The average cross-section and placement of the nanostructures, including **213** and **214**, may depend on processing variables, such as the extent of etching and the load applied to modulate and control nanostructure size. Furthermore, the size and placement of the nanostructures may depend on the geometry, such as the sidewall slope, of the raised and recessed regions **5** and **6** and the technique used to separate the stamp **7** from the supporting substrate **9**.

[0048] Local chemical and physical forces acting at the interfaces between the supporting substrate **9** and the nanostructure **214**; between the stamp **7** and the nanostructure **214**; and between the stamp **7** and the nanostructure **213**, for example, also may direct placement of nanostructures. Local chemical and physical forces may include magnetic forces, electrostatic

forces, dipole-dipole forces, van der Waals forces, and mechanical forces. Upon separation of the stamp **7** from the supporting substrate **9**, these and other local forces may determine whether the fabricated nanostructures remain on the supporting substrate **9**, and/or on the stamp **7**, and/or embedded in the recessed regions of the stamp **7**. The structures **210**, **220**, **230**, **240**, **250**, and **260** provide examples of how the presently claimed invention can form a plurality of unique nanostructures from a single stamping procedure.

[0049] The structure **210** illustrates the type of nanostructures that may be fabricated when etching has not completely removed portions of the film **8** at the contact **10**. By controlling etching in this manner, the nanostructures **214** may be fabricated. Because stronger local forces exist between the nanostructure **214** and the supporting substrate **9** than between the nanostructure **214** and the stamp **7**, when separated, the nanostructure **214** remains on the supporting substrate **9**.

[0050] The structure **220** illustrates the type of nanostructures that may be fabricated when etching has not completely removed the film **8** from the recessed region **6** of the stamp **7**. In this aspect, the nanostructure **213** is fabricated. Because stronger local forces exist between the nanostructure **213** and the stamp **7**, than between the nanostructure **213** and the supporting substrate **9**, when separated, the nanostructure **213** remains embedded within the recessed region **6** of the stamp **7**.

[0051] The structure **230** illustrates the type of nanostructures that may be fabricated when etching has not completely removed portions of the film **8** from the contact **10** and from the recessed region **6** of the stamp **7**. Because stronger local forces exist between the resulting nanostructure **213**, **214** and the supporting substrate **9**, than between the nanostructures **213**, **214** and the stamp **7**, when separated, the nanostructures **213**, **214** remain on

the supporting substrate **9**. Similarly, the structure **240** illustrates the type of nanostructures that may be fabricated when incomplete etching at the contact **10** and the recessed region **6** is coupled with stronger local forces existing between the nanostructures **213**, **214** and the stamp **7**. The structures **250** and **260** illustrate the type of nanostructures that may be fabricated when incomplete etching at the contact **10** and the recessed region **6** is coupled with strong local force existing between the nanostructure **213** and the supporting substrate **9** and between the nanostructure **214** and the stamp **7**.

[0052] **FIG. 3** illustrates an exemplary procedure illustrating the use of a stamp assembly **300** that includes an embedded nanostructure **313** as a mask for photolithography. The stamp assembly **300** may be placed on a photoresist **318**. The stamp assembly **300** may include a transparent stamp **307** and an opaque nanostructure, such as the nanostructure **313**. When radiation **315** is introduced to the stamp assembly **300**, the opaque nanostructure **313** of the stamp assembly **300** substantially prevents a portion of the radiation **315** from reaching the photoresist **318**. Thus, the chemical or physical change that the radiation **315** would otherwise bring about at the surface of the photoresist **318** does not substantially occur in the regions under the nanostructure **313**. In the areas of the photoresist **318** not protected by the nanostructure **313**, the radiation **315** may bring about chemical or physical changes that may make the irradiated portions of the photoresist **318** more or less prone to dissolution, further chemical reaction, and the like.

[0053] For example, if irradiation makes the photoresist **318** more susceptible to dissolution, removing the irradiated portions of the resist can lead to a pattern on substrate **319**, which resembles the structure or pattern of the nanostructure **313**. A working distance **317**, defined as the distance between the surface of the photoresist **316** and the surface of the stamp

assembly **300**, can be adjusted with a stepper, micropositioner, or piezoelectric translator. The approximately coplanar arrangement of the nanostructure **313** with the surface of the stamp **307** allows a very small working distance **317** to be achieved by placing the stamp assembly **300** on the resist **318**. In this aspect, the stamp assembly **300** may be used as a close proximity photomask.

[0054] A multiplicity of structures and nanostructures, including those illustrated in **200**, **210**, **220**, **230**, **240**, **250**, and **260** of **FIG. 2**, may be preferably used as masks for lithographic techniques, including X-ray and EUV photolithographies, for example. When the substrate **319** is flexible, such as if made from a flexible polymer, the substrate **319** may function as a low-cost 1:1 X-ray photomask. Preferably, the working distance between the photomask and the material to be patterned is less than 5 μm. Larger working distances may be preferred when diffraction effects are desirable to form more complex patterns.

[0055] In another aspect, the nanostructure **313** can interact with the radiation **315**, which may permanently or transiently alter the chemical or physical properties of the nanostructure **313**. By altering the properties of the nanostructure **313**, a chemical or physical change may be induced in the resist **318**. For example, if the stamp assembly **300** is in contact with the resist **318** when the radiation **315** is applied, local heating of the nanostructure **313** may occur. This local heating can selectively transfer heat to the regions of the resist **318** that are in direct contact with the nanostructure **313**. The selectively heated regions of the resist **318** may undergo chemical or physical changes that enable the selectively heated regions to selectively dissolve, and the like. While other types of radiation are possible for selective heating, microwave, infrared, radio frequency, or combinations thereof are preferred.

[0056] **FIG. 4** illustrates an exemplary procedure for the directed transfer of nanostructures **414** to a support **419**. Stamp **407** includes the nanostructures **414** residing on the raised regions **405** of the stamp **407.** Directed transfer of the nanostructures **414** onto the support **419** may be accomplished by moving the stamp **407** into and then out of contact with the support **419**.

[0057] Which nanostructures transfer to the support **419** may be controlled by selecting the materials and methods so that stronger local forces exist between the nanostructures desired for transfer and the support **419** than between the nanostructures and the stamp **407**. For example, the nanostructure **213,** as shown in structure **220** of **FIG. 2**, may be transferred to the support **419** if the adhesive interaction acting between the support **419** and the nanostructure **213** is greater than the adhesive interaction acting between the stamp 7 and the nanostructure **213**.

[0058] In **FIG. 4**, stronger local forces are present between the support **419** and the nanostructures **414** than between the nanostructures **414** and the stamp **407**. Thus the nanostructures **414** remain on the support **419**. While not shown in **FIG. 4**, the nanostructures for transfer also may reside within the recessed regions **406** or may simultaneously reside on the raised regions **405** and within the recessed regions **406** of the stamp **407**. In this manner, nanostructures may be created on one surface, for example the stamp **407**, and then transferred to another surface, for example the support **419**. Alternatively, other methods may be used to transfer the nanostructure **414** from the stamp **407**, such as selectively dissolving the stamp **407** while it is in contact with the support **419**, and the like.

[0059] The nanostructures and nanostructure fabrication methods of the presently claimed invention may be utilized to form many nanoscale materials. In one aspect, spectroscopic reference materials, such as for

surface enhanced Raman spectroscopy, for example, may be fabricated. In another aspect, single and multi-layer photonic materials may be fabricated for use as X-Ray lithography masks, band gap structures, gratings, and optical filters. In another aspect, various patterning processes may be accomplished, including, pattern transfer to polymers and fiber optic patterning accomplished by the directed transfer of nanostructures.

[0060] The directed transfer of nanostructures may be combined with insulators, semiconductors, and metals to fabricate integrated circuits, display components, or catalysts, for example. Furthermore, the claimed devices and methods may be used functionalize the surface of various materials so they may be adapted for use as sensors, sensor arrays, optical reference materials, electrochemistry test structures, electrodes for displays, or light emitting diodes, for example. The claimed devices and methods may also be utilized in medical devices, such as in the formation of microarray chips for DNA, RNA, nucleic acids, proteins and antibodies. They may also be beneficially used to form microchannels for chemical reactors assays and sensors on chips, i.e. "lab on a chip" devices.

[0061] The preceding description is not intended to limit the scope of the invention to the preferred embodiments described, but rather to enable a person of ordinary skill in the art of nanostructure fabrication to make and use the invention. Similarly, the examples below are not to be construed as limiting the scope of the appended claims or their equivalents, and are provided solely for illustration. It is to be understood that numerous variations can be made to the procedure below, which lie within the scope of the appended claims and their equivalents.

EXAMPLES

[0062] Example 1: Formation of A Polystyrene Stamp

[0063] Polystyrene (PS) having a molecular weight average of 235,000 g/mol. was obtained from Scientific Polymer Products Inc. (Ontario, New York). The PS elastomeric stamp/polymer grating used for contact restricted etching and adhesive transfer of gold (Au) was molded from a "saw tooth" silicon grating (TGG01) obtained from K-TEK International Inc. (Portland, OR). The silicon grating occupied a (3×3) mm^2 area possessing a feature dimension **537** of ~3 μm, such as shown in **FIG. 5a**. Sidewall slope **540** of the "t ooth" is depicted as a dashed line in **FIG. 5a**. The silicon grating was placed face up in an aluminum or TEFLON holding cell with ~0.5 g of PS placed over the grating. The cell was then heated to 210° C for ~2 hours and allowed to cool to room temperature. The PS stamp was then separated from the silicon grating with brief sonication (< 1 min.) in methanol.

[0064] Example 2: Formation of a Polycarbonate Stamp

[0065] The metallic layer of a commercially available compact disc (CD) was delaminated by scoring the CD surface and then vigorously rinsing with ultrapure water. The recording media was removed with a rapid methanol rinse followed by brief sonication (~30 sec.) in a 1:4 (v/v) methanol/water solution and a final rinse in ultrapure water. The CD stamps had a " rectangular" grating structure possessing a feature dimension **537** of ~1.6 μm, such as shown in **FIG. 5b**. The rectangular CD stamps also possess raised region features with a feature dimension **535** of ~ 1.0 μm as well as recessed region features with a feature dimension **536** of ~ 0.6 μm.

[0066] Example 3: Formation of a Film Coated Supporting Substrate

[0067] A 70 to 300 nm Au film was sputter coated onto a supporting substrate using a BAL-TEC MED 020 sputter coater (Liechtenstein). The Au (99.99% purity) was obtained from Techno Trade International (Manchester, NH). Supporting substrates coated with Au included freshly cleaved muscovite mica (Structure Probe Inc., West Chester, PA), glass cover-slips, glass slides, Si(100) wafer, and Si(100) wafer with a chemisorbed self-assembled monolayer (SAM) of octadecyl triethoxysilane (Gelest Inc., Morrisville, PA). Si(100) wafers were obtained from Virginia Semiconductor (Fredericksburg, VA). A gold coated supporting substrate resulted.

[0068] Example 4: Film Compression

[0069] The Au coated supporting substrate from Example 3 was placed in conformal contact with the stamp of Example 1 or 2 and held together between two compression plates in a TEFLON compression cell. The compression cell is illustrated in **FIGs. 6** and **7** and may include external plates, machine screws, and nuts made from a fluoropolymer, such as TEFLON. The cell may be obtained from Craftech Industries Inc., Hudson, NY. Two different compression plates, specifically planar compression plates **602** and curved compression plates **702**, were used during nanowire fabrication. Newton' s rings (interference fringes) and contact area (a) were used to optically qualify proper mating of the compression plates with the surface of the stamp and the supporting substrate.

[0070] **FIG. 6** illustrates a compression cell **601** equipped with planar compression plates **602**. While any suitably planar material may be used to form the compression plates **602**, glass slides and glass cover cover-slips are presently preferred. The compression plates **602** may distribute the compression force in a substantially uniform manner against a polymer stamp

607 and a supporting substrate **609**. In this manner, nanostructures having substantially similar average cross-sections may be formed from a gold film **608** deposited on the supporting substrate **609**.

[0071] **FIG.** 7 illustrates a compression cell **701** equipped with the curved compression plates **702**. Two convex lenses (possessing a radius of curvature of about 49 mm) may be utilized as the curved compression plates **702** to compress a polymer stamp **707** and a supporting substrate **709** against a film **708**. The film **708** may be gold deposited on a supporting substrate **709** that includes mica. The curved compression plates **702** may provide a better-controlled point of contact with the stamp **707** and the supporting substrate **709**.

[0072] In one aspect, a better-controlled point of contact permitted quantification of the contact radius (a), from which the normal load and pressure was estimated with Hertz contact mechanics theory. Using the curved compression plates **702** in combination with the polymer stamp **707** having "saw to oth" geometry, such as a stamp of the type illustrated in **FIG. 5a**, enabled production of nanostructures whose widths had a radial dependence.

[0073] The radial dependence and pressure distribution of the nanostructure widths were found to approximate what was predicted by Hertz theory. Thus, nanostructures may be fabricated with average cross-sections that increase or decrease in size as they move away from a central point, where a greater or lesser force, respectively, is exerted against the stamp **707**. By varying the shape of the compression plates **702**, it may be possible to control the average cross-sections and/or shape of the resultant nanostructures using a single stamp.

[0074] Prior to compression of the polymer stamp **607** or **707** against the substrate supported gold film, **608** or **708,** the contact surfaces of the Au film and the polymer stamp were wet with a liquid, such as methanol (Fisher) or water. This pre-wetting suppressed bubble formation and reduced the surface tension between the water based etchant and the hydrophobic polymer stamp.

[0075] <u>Example 5: Film Etching</u>

[0076] After compression of the polymer stamp **607**, **707** against the substrate supported film **608**, **708**, the compression cell was immersed in a 500 mL polycarbonate container and ~120 ml of gold etchant solution was added. Transene gold etchant TFA (Danvers, MA) was diluted with ultrapure H_2O (EASYpure RF, 18.2 MΩ·cm) to increase or decrease the rate of gold etching. The volume/volume dilution ratio of TFA gold etchant to H_2O ranged from 1:1 to 1:12.5 (v/v). The etching reaction was allowed to proceed at room temperature (22 ± 3° C) or was heated (preferably less than 75° C) with rapid stirring for ~4-72 hours. The duration of the reaction depends on the concentration of etchant and the temperature used.

[0077] Once the etching process has reached the desired level of completion, the stamp was removed with or without addition of a solvent, such as methanol or water, to again reduce the surface tension and facilitate separation of the two surfaces without disturbing the resulting gold nanostructures. The polymeric stamp and substrate were then gently rinsed with ultrapure H_2O and dried under vacuum.

[0078] <u>Example 6</u>: Synthesis of Nanowires

[0079] When a stamp having rectangular geometry, such as a stamp of the type illustrated in **FIG. 5b**, is used, nanowires having an ~400 nm

diameter were formed with a 1:2 (v/v) dilution of TFA gold etchant in H_2O with a 41 hour reaction time at 22° C and a subsequent heating for 13 hours at 65° C. Also for a rectangular stamp, nanowires having an ~800 nm diameter were formed using a 1:2 (v/v) dilution of TFA gold etchant in H_2O with a 50 hour reaction time at 70° C.

[0080] Example 7: Characterization of Fabricated Nanostructures

[0081] SEM images of the resulting nanostructures (type **213** and **214** from **FIG. 2**) on the polymer stamp and supporting substrate were obtained with an Amray 1800 SEM (Amray Inc.).

[0082] **FIG. 8** is an SEM image of the nanostructures formed in accordance with the present invention. Specifically, two separate arrays of Au nanowires, the first embedded in the recessed regions, the second on the raised regions, of two rectangular polycarbonate stamps were fabricated as a binary array. Regarding the first stamp, ~800 nm nanowires **810** were formed, while on the second stamp, ~400 nm nanowires **820** were formed. The image shows the ~800 nm nanowires **810** embedded in the recessed regions of the first stamp and the raised regions **805** of the first stamp. The ~400 nm nanowires **820** were transferred, such as by the method described with regard to **FIG. 4**, onto the surface of the ~800 nm nanowires **810** at an approximate 90° angle to create a nanowire "crosshatch" pattern on the first stamp.

[0083] **FIGs. 9a** and **9b** are SEM images of 3-layered crosshatch nanostructures. **FIG. 9a** is a near-field image depicting a 1 μm square area of the nanostructure depicted in the far-field image of **FIG. 9b**. Three separate procedures yielded the pictured gold arrays. The first layer of nanowires may be seen repeating along line **910** of **FIG. 9a**. The second layer of nanowires may be seen repeating along line **920** of **FIG. 9a**. The third layer of

nanowires may be seen repeating along line **930** of **FIG. 9a**. The second and third layers were successively transferred onto the surface of the stamp, which included the first layer of nanowires.

[0084] The first layer nanowires were formed in the recessed regions of a first rectangular polycarbonate stamp by etching with a 1:12.5 (v/v) solution of TFA gold etchant in H_2O for 24 hours at 22° C. The nanowires that form the second layer were formed in the recessed regions of a second rectangular polycarbonate stamp and were transferred onto the nanowires residing in the recessed regions of the first polycarbonate stamp. The second layer nanowires were formed in the second stamp by etching with a 1:2 (v/v) solution of TFA gold etchant in H_2O for 44.5 hours at 22° C. The nanowires that form the third layer were formed in the recessed regions of a third rectangular polycarbonate stamp and were transferred onto the second layer of nanowires. The third layer nanowires were formed in the third stamp by etching with a 1:2 (v/v) solution of TFA gold etchant in H_2O for 43.5 hours at 22° C and for 1.5 hours at 65° C.

[0085] **FIG. 10** is an SEM image of a binary gold nanowire array. A rectangular polycarbonate stamp was used to form ~900 nm nanowires **1013** residing in the recessed regions of the stamp and ~130 nm nanowires **1014** residing on the raised regions of the stamp. Both sets of nanowires were simultaneously formed by etching with a 1:12.5 (v/v) dilution of TFA gold etchant in H_2O for 24 hours at 22° C.

[0086] **FIG. 11** is an SEM image of a nanostructure including a gold nanowire array and colloidal polystyrene spheres. A compression cell equipped with curved compression plates was used with a saw tooth stamp to produce the array. After compression of the gold film, etching was conducted with a 2:3 (v/v) dilution of TFA gold etchant in H_2O for 48 hours

at 70° C to form ~200 nm gold nanowires **1114** residing on the raised regions of the saw tooth polystyrene stamp. Colloidal polystyrene spheres **1150**, having average diameters of ~ 200 nm, were solution deposited into the recessed regions of the stamp. The SEM image established that the Au nanowires resided on the raised regions of the stamp.

[0087] **FIG. 12** includes SEM images establishing that the pressure distribution and geometric etch anisotropy can be used in combination to radially modulate the average cross-sections of the formed nanostructures. A compression cell equipped with curved compression plates was used with a saw tooth stamp to produce the gold nanowire array. After compression of the gold film, etching was conducted with a 2:3 (v/v) dilution of TFA gold etchant in H_2O for 48 hours at 70° C. The SEM images **1200-1240** reveal a radial variation of the average cross-section of the Au nanowires. The images show the gradual average cross-section width increase of the nanowires **1205** from ~180 nm at the outer edge of the stamp – film contact, to nanowires **1245** having an average cross-section width of ~900 nm at the contact center where the largest force is applied to the stamp by the curved compression plates. Colloidal polystyrene spheres **1250** established that the Au nanowires resided on the raised regions of the stamp.

[0088] As any person of ordinary skill in the art of fabrication of nanostructures will recognize from the provided description, Figures, and examples, modifications and changes can be made to the preferred embodiments of the invention without departing from the scope of the invention defined by the following claims and their equivalents.